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Electronic and atomic structures of the Ag induced $\sqrt{3} \times \sqrt{3}$ superstructure on Ge(111)

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ABSTRACT

The Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ surface together with Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ constitutes a set of surfaces that is ideally suited for fundamental studies related to low dimensional physics. We here focus on the atomic and electronic structures of the two-dimensional $\sqrt{3} \times \sqrt{3}$ superstructure induced by Ag on Ge(111), a surface that is significantly less studied than the Si counterpart. Extensive information on the surface band structure obtained by angle resolved photoelectron spectroscopy (ARPES) is presented, complemented by atomic information from scanning tunneling microscopy (STM). The results reveal new findings that are important for the understanding of the Ag induced $\sqrt{3} \times \sqrt{3}$ structure, acting as a prototype for semiconductor/metal interfaces. i) We have identified a new occupied surface band near the $\overline{M}$-point of the $\sqrt{3} \times \sqrt{3}$ surface Brillouin zone. ii) The Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ surface exhibits a partially occupied surface band, S_1, with a parabolic-like shape at $\overline{\Gamma}$. At low temperature (LT) this band splits into two bands, S_{1U} and S_{1D}. The identification of two bands is significantly different from the case of Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ for which just one band has been reported. Besides these specific results, our extensive ARPES study reveals four surface bands at room temperature (RT), while five surface bands were identified at ≈100 K (LT). Room temperature empty state STM images show, depending on the tunneling bias, both honeycomb and hexagonal periodicities which are consistent with the honeycomb chained trimer and the in-equivalent trimer models, respectively.

1. Introduction

Semiconductor surfaces with metallic adsorbates exhibit well-ordered two-dimensional (2D) structures that are fundamentally important since various physical phenomena can be observed which contain rich science. Phase transitions, metal-insulator and metal–semiconductor transitions, charge density waves, and domain wall structures are examples of subjects that have been studied [1–10]. In addition, these systems provide an ideal 2D platform for the study of surface electronic and atomic structures. Silver (Ag) and gold (Au) are examples of metallic adsorbates that can induce several 2D structures [11,12]. Especially Ag on elemental semiconductor surfaces, such as Si(111), has been used as a prototype element to modify the atomic and electronic properties [8,11–16]. These investigations have been concentrated to one monolayer (ML) of Ag on Si(111), i.e., the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ superstructure [13–33] covering quite many properties of the surface, such as, atomic and electronic structures, surface conductivity, Fermi surfaces, electron group velocity, substrate band bending and the Hall effect, among others [13–33]. The Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface shows an increased conductivity upon exposure to a tiny amount of noble or alkali metals [13,14,26,27,34,35]. The four point probe technique has been introduced to measure the conductivity and resistivity on such surfaces [15,36–39]. A similar $\sqrt{3} \times \sqrt{3}$ superstructure is formed by 1 ML of Ag on Ge(111) [7,40–44]. The atomic structure of this surface is believed to be described by the honeycomb chained trimer (HCT) and/or the in-equivalent trimer (IET) model as for the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface [43,44]. Surprisingly, the electronic structure of Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ has not yet been studied in detail and just a few references [7,41,42] give some information about the surface bands and then just along one symmetry line of the $\sqrt{3} \times \sqrt{3}$ surface Brillouin zone (SBZ). Therefore, it is worth to explore the electronic structure of Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ in detail, at both room temperature (RT) and low temperature (LT).

In the present study, Ag/Ge(111) $\sqrt{3} \times \sqrt{3}$ surfaces were formed after initial depositions of two different amounts of Ag, i.e., 0.9 and 1.1 ML, onto the clean Ge(111)c(2 × 8) surface. These two preparations facilitated a study of the influence of extra Ag atoms on the surface band structure. This is particularly important when it comes to a partially occupied surface band, S_1, also observed for Ag/Si(111) $\sqrt{3} \times \sqrt{3}$. Detailed surface band dispersions are presented along the $\overline{\Gamma}-\overline{M}-\overline{\Gamma}$ and $\overline{\Gamma}-\overline{K}-\overline{M}$ high symmetry lines of the $\sqrt{3} \times \sqrt{3}$ SBZ obtained at RT and at ≈100 K (LT) for both the 0.9 and 1.1 ML Ag cases. Four surface bands were found

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in the RT data, while five surface bands were identified at LT. Of these bands, the three completely occupied ones do not change with temperature or Ag amount. Interestingly, one of these bands has not been reported before. The existence of the band is verified for the two Ag amounts, the two temperatures, and for the three photon energies used in this study. Another new result is related to the behavior of the partially occupied S_1 band at $\bar{\Gamma}$. At low temperature ($\approx$100 K) this band splits into two bands, S_{1U} and S_{1D}. The identification of two bands is significantly different from the case of Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ for which just one band has been reported. The S_1, S_{1U} and $S_{1D,}$ bands are discussed based on both RT and LT data for the two Ag coverages. Atomic structure information from the Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ surface was obtained by STM. Depending on the tip to sample bias, the STM images were in agreement with the HCT or the IET model [43,44].

2. Experimental details

All electronic structure studies were performed at beamline I4 located at the MAX-III storage ring of the MAX-lab synchrotron radiation facility in Lund, Sweden. The photoemission data presented in this paper were obtained at photon energies of 21.2, 30, and 40 eV. The major part of the photoemission data was obtained at 30 eV with a total energy resolution of $\approx$30 meV, and an angular resolution of 0.3°. There are two UHV chambers at the experimental station, one for surface preparation equipped with a sputter gun, quartz crystal thickness monitor, residual gas analyzer, low energy electron diffraction (LEED) optics, and an Ag evaporator, while the second chamber is equipped with a LEED optics and a SPECS Phoibos 100 electron analyzer with a 2D detector. The chambers had base pressures of less than 1×10^{-10} Torr, while during the Ag evaporation the pressure in the preparation chamber was $<4\times10^{-10}$ Torr. The substrate was cut from an n-type Ge(111) wafer doped with Sb, with a resistivity in the range 7–10 Ωcm at room temperature. The Ge(111) substrate was degreased *ex-situ* using acetone and isopropanol and cleaned *in-situ* by multiple Ar^+–ion sputtering (1 keV) and annealing (730 °C) cycles in order to produce a well-ordered Ge(111)c(2 × 8) surface as verified by LEED. A quartz crystal thickness monitor was used to establish the Ag evaporation rate, i.e., 0.4 ML/min in our case. Surfaces were prepared by evaporating two different amounts of Ag, i.e., 0.9 and 1.1 ML (1 ML is defined as the density of atoms on the unreconstructed Ge(111) surface, i.e., 7.2×10^{14} atoms/cm^2), in order to facilitate an investigation of the effect of additional Ag atoms. Subsequent post annealing of the surfaces up to 330 °C for a few minutes, resulted in well-ordered Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ superstructures in both cases. The preparation based on 1.1 ML of Ag ensures that the $\sqrt{3}\times\sqrt{3}$ superstructure is fully developed, i.e., there are no signs of c(2 × 8) or 4 × 4 domains in LEED patterns or STM images. However, there are extra Ag atoms freely moving on the surface at room temperature on the surface prepared this way. The number of these Ag atoms can be reduced by annealing, but it is hard to completely remove them as reported in earlier studies [7,23]. The surface with 0.9 ML of Ag was prepared in order to significantly reduce the number of extra Ag atoms. As a consequence of the less than optimal amount of Ag, the surface showed 4 × 4 diffraction spots and streaks in LEED. As expected, the dominating $\sqrt{3}\times\sqrt{3}$ areas had a lower number of additional Ag atoms which had a significant effect on the electronic structure.

An investigation of the surface atomic structure was performed in a separate UHV chamber equipped with a LEED optics, a sputter gun, an Ag evaporator, a quartz crystal thickness monitor, and an Omicron variable-temperature scanning tunneling microscope (VT-STM), situated at Linköping University, Sweden. The VT-STM uses an electrochemically etched W-tip cleaned in-situ by electron beam heating. The surface preparation methods were the same as those described above for the two Ag coverages (0.9 and 1.1 ML). All STM measurements were performed at room temperature in the constant current mode (100 pA).

3. Results and discussion

3.1. Atomic structure

In Fig. 1, we present LEED and STM results from the two Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ surfaces prepared by depositing 0.9 and 1.1 ML of Ag, respectively. With an Ag coverage of 0.9 ML the LEED pattern shows streaks and 4 × 4 diffraction spots (Fig. 1(a)), while the 1.1 ML preparation exhibits only well-defined $\sqrt{3}\times\sqrt{3}$ diffraction spots (Fig. 1(b)). The large scale (150 × 150 nm^2) empty state STM images in Figs. 1(c) and 1(d) present the 0.9 and 1.1 ML cases, respectively. Fig. 1(c) shows small patches of the 4 × 4 structure (indicated by arrows) on a surface that is dominated by the $\sqrt{3}\times\sqrt{3}$ periodicity. In the 1.1 ML case, Fig. 1(d), there is no trace of any other structure than $\sqrt{3}\times\sqrt{3}$.

Figs. 2(a) and 2(b) show small scale ($\approx$6.4 × 6.4 nm^2) empty state images obtained at a sample bias of 0.3 and 1.0 V, respectively. At the 0.3 V bias the image shows an apparent honeycomb structure while at 1.0 V the image has a strong hexagonal appearance. The honeycomb pattern has been explained by the honeycomb-chained-trimer (HCT) model (Fig. 2(c)) which was considered to describe the atomic structures of Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ and Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ at RT for a long time [18,40,43]. The positions of the bright protrusions observed by STM, forming the honeycomb pattern, correspond to the centers of Ag trimers, while the dark center of a honeycomb corresponds to the center of a Si or Ge trimer, respectively. Later, another model, the in-equivalent trimer (IET) model (Fig. 2(d)), was proposed for the Ag/Si(111) $\sqrt{3}\times\sqrt{3}$ surface to explain the hexagonal structure observed by STM at low temperature [19–21,32]. Due to the two trimers being in-equivalent one becomes brighter than the other in the STM image resulting in a hexagonal pattern as that of Fig. 2(b). Recently, the same type of model has been suggested for the Ag/Ge(111) $\sqrt{3}\times\sqrt{3}$ surface as well [44].

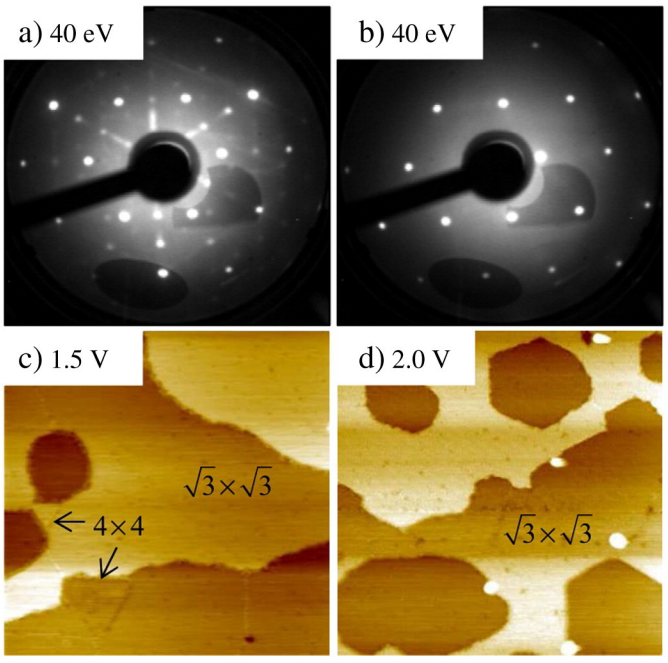

Fig. 1. (a) LEED pattern of the $\sqrt{3}\times\sqrt{3}$ surface prepared by 0.9 ML of Ag. Besides $\sqrt{3}\times\sqrt{3}$, there are streaks and additional 4 × 4 spots. (b) In the case of 1.1 ML of Ag the LEED pattern only exhibits $\sqrt{3}\times\sqrt{3}$ diffraction spots. The LEED patterns in (a) and (b) were obtained at an electron energy of 40 eV. (c) and (d) Large scale (150 × 150 nm^2) empty state STM images obtained at RT from the 0.9 and 1.1 ML surfaces, respectively. The images were recorded in constant current mode (100 pA) at a bias of 1.5 V in (c) and 2.0 V in (d).